（ 続紙 1 ）

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論文題目	Rejection Properties of Perfluorohexanoic Acid in Various Aqueous Media by Polyamide and Sulfonated Polyethersulfone Nanofiltration Membranes（ポリアミドおよびスルホン化ポリエーテルスルホン系 NF 膜による種々の水溶液中のペルフルオロヘキサン酸の除去特性に関する研究）		

This thesis presents the research work on rejection properties of perfluorohexanoic acid (PFHxA) in various aqueous media by polyamide and sulfonated polyethersulfone nanofiltration membranes.

Chapter 1 introduction describes the background of this study that motivates to carry out this study, objectives and the thesis structure.

Chapter 2 reviews past researches related to the research topic. The basic information of per- and polyfluoroalkyl substances (PFASs) is provided, such as their physicochemical properties, applications in industries, occurrences in the environment, toxicity and the regulations and legislations on the use and production of PFASs. In addition, removal techniques for PFASs from wastewater and drinking water are introduced, including membrane filtration, adsorption process and UV photolysis. At last, the fundamentals of nanofiltration are presented, including their basic structures and factors affecting its separation efficiency and membrane fouling.

Chapter 3 presents the research work on rejecting PFHxA in pure water at trace level (100 – 300 ng/L) by membranes. To reduce the exposure risk for human to PFHxA in tap water, effective technique for rejecting PFHxA in drinking water should be developed as conventional drinking water treatment process is not effective on PFHxA removal. In this chapter, three kinds of membranes have been tested, including one reverse osmosis (RO), two nanofiltration (NF) and two ultrafiltration (UF) membranes. The highest PFHxA rejection rate was found with RO membrane (99.18%), which was due to its smallest pore size among all tested membranes. Two NF membranes showed comparatively good PFHxA rejection rates (95.31% and 96.28%, respectively) with RO membrane, while it offered a much higher water flux. Additionally, their lower salt rejection rate suggested higher passage of minerals in drinking water treatment, which is good for supplied water quality. Thus, their application might be better options for rejecting PFHxA in drinking water treatment. Furthermore, it was also found that rejection rate of PFHxA might be not just dependent on the molecular weight cut-off (MWCO) of membrane. The surface charge of NF membranes (zeta-potential) might also play an important role in the rejection of PFHxA.

In chapter 4, two kinds of nanofiltration membranes (NF 270 and NTR-7450) made from different materials were investigated on rejection properties of PFHxA in aqueous solution. Results suggested that these membranes have different rejection properties to PFHxA. For polyamide NF membrane (NF270), its rejection rate to PFHxA was sensitive to the change of feed water pH, but its membrane flux kept stable when changing feed water pH. Opposite results were obtained with sulfonated polyethersulfone NF membrane (NTR-7450). It had a high stability on PFHxA rejection rate, while its water flux was very sensitive to the change of feed water pH. The different rejection properties between these NF membranes could be explained by differences of the materials of their selective layer. NF 270 was made from

polyamide, whereas NTR-7450 was made from sulfonated polyethersulfone. These two materials have different functional groups, which caused different responses to the change of feed water pH. The findings reported in this chapter would be useful for the membrane selection in practical applications.

Chapter 5 shows the investigation on the rejection of PFHxA in industrial wastewater by two NF membranes (NF 270 and NTR-7450). NF 270 was found to have better performance on rejecting PFHxA in industrial wastewater in terms of membrane flux and PFHxA rejection rate. The characterization of these two membranes suggested that NF 270 has smaller pore size but higher porosity than NTR-7450. This is the reason why NF 270 showed a better rejection performance on PFHxA. However, more severe membrane fouling was also observed with this membrane, which could be inferred from its more rapid flux decline. This indicates that proper measures should be taken to alleviate the membrane fouling once NF membranes were applied for PFHxA recovery from industrial wastewater. In addition, the effect of pH and salt on the rejection of PFHxA by NF 270 was also examined, and it was found that PFHxA rejection performance could be enhanced by increasing feed water pH, while four kinds of salts (NaCl, Na_2SO_4, $CaCl_2$ and $CaSO_4$) tested did not show any significant impact on the rejection of PFHxA, which was quite different from rejection of other kinds of PFASs by NF membranes (e.g. PFOS). This suggested that salts may impact the rejection efficiency of PFASs with different carbon chain length through different way.

Chapter 6 gives a summary for the whole thesis. Recommendations for further research had also been given out, such as scaling up the membrane filtration system from lab scale to bench scale, development of proper pretreatment methods to alleviate the membrane fouling and development of methods for the final disposal of the PFHxA in concentrate.

（続紙 ２ ）

氏 名	曾　　程 輝

（論文審査の結果の要旨）

本論文は、新規残留性有機汚染物であるポリ-及びペルフルオロアルキル物質（PFASs）の中で、最近とくに製造量・使用量が増大してきているペルフルオロヘキサン酸（PFHxA）を対象として、膜濾過による除去特性を検討したものである。そのため、水道原水を模した人工試料、PFHxA を含む実際の工場廃水を対象として、各種の濾過膜で実験を行い、その除去特性を検討した。主要な成果は下記の通りである。

(1) 浄水場での除去を想定し、PFHxA を微量濃度（100～300 ng/L）で含む模擬水道原水試料に対し、１種類の逆浸透膜、２種類のナノ濾過膜、２種類の限外濾過膜による平膜クロスフロー連続実験を実施して、それぞれ>99%、95%、96%、69%、84%の除去率を得た。PFHxA 分子量 338 よりも高い排除分子量（各々3000 と 1000）のナノ濾過膜でもきわめて高い除去率が得られたことより、物理的阻止以外の除去メカニズムが働いていることが示された。そこで膜表面のζ電位を測定し、電気的な排除メカニズムが生じている可能性を見出した。これにより浄水場での対策としてナノ濾過膜の適用性が示唆された。

(2) ２つの異なるナノ膜（ポリアミド系とスルホン化ポリエーテルスルホン系）で PFHxA 除去性能を比較した実験より、両者で試料水 pH 依存性が異なる結果が得られた。ポリアミド系ナノ膜（NF270）は低 pH で除去性能が低下したが、スルホン化ポリエーテルスルホン系ナノ膜（NTR-7450)では高い除去性能を維持し、膜材質が PFHxA のナノ膜の濾過特性に大きく影響することが示された。

(3) PFHxA を含む実際の工場廃水に対するナノ濾過の実験を NF270 と NTR-7450 との２つの濾過膜を用いて実施した。NF270 は NTR-7450 より高い除去性能を示したが、より早く目詰まりを生じた。さらに NF270 で廃水中の pH と陽イオン（Ca^{2+}と Na^{+}）の影響を調べたところ、前者は pH5 以下で大きく PFHxA の除去率が低下するが、後者はほとんど影響がないことが示された。これらの事実より、工場廃水中の PFHxA のナノ濾過処理においては、濾材材質と廃水特性との両者を考慮して適用する必要があることを見出した。

以上のように本論文は、将来、汚染対策がますます重要となる可能性の高いペルフルオロヘキサン酸（PFHxA）について、浄水処理および工場廃水処理でのナノ濾過膜の可能性を実験的に検証したものであり、今後の水環境保全、水処理技術開発に大きく貢献するものであって 、学術上、実際上寄与するところが少なくない。よって、本論文は博士（工学）の学位論文として価値あるものと認める。また、平成２９年８月２４日、論文内容とそれに関連した事項について試問を行って、申請者が博士後期課程学位取得基準を満たしていることを確認し、合格と認めた。

なお、本論文は、京都大学学位規定第１４条第２項に該当するものと判断し、公表に際しては、当該論文の全文に代えてその内容を要約したものとすることを認める